

# Quarterly Technical Report

## Selected Energy Epitaxial Deposition and Low Energy Electron Microscopy of AlN, GaN and SiC Thin Films

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Epitaxial AlN films were grown on as-received and hydrogen etched 6H-SiC(0001) substrates using an ammonia supersonic seeded beam. The films on the latter substrates exhibited a higher degree of order. Cross-sectional electron microscopy revealed sharper SiC-AlN interfaces with extended flat terraces. The few stacking mismatch boundaries originated from the 1.5 nm steps corresponding to the 6H stacking sequence. *In situ* LEEM/LEED studies were conducted on GaN homoepitaxial growth on MOCVD GaN substrates by plasma-assisted gas-source MBE. After 6 hours of growth at 660°C, LEEM images showed a GaN layer with a hexagonal parquet structure and a large number of dark spots on the surface. *Ex situ* AFM studies revealed that the former was a result of spiral growth and the latter were due to surface pits of hexagonal shape. The surface density of the pits is  $1-2 \times 10^9 \text{ cm}^{-2}$ . *In situ* cleaning of MOCVD-grown GaN/AlN/6H-SiC substrates using  $\text{NH}_3$ -seeded supersonic molecular beams was investigated. Complete oxygen removal was achieved by heating in vacuum at 730°C. Surface carbon concentrations of ~3%, as evidenced by XPS, were achieved by heating at 730°C under a hyperthermal  $\text{NH}_3$  flux. Modifications have been made to the SEE system to provide a cleaner vacuum ambient and are detailed in this report. A new substrate holder was fabricated that uses Mo clips and a polished Mo block to ensure good thermal contact without Ag paste. Outgassing of the colloidal Ag paste is believed to be one source of carbon contamination at high temperatures. The design of the N plasma source and testing chamber is also reported.

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## I. Introduction

The realized and potential electronic applications of AlN, GaN and SiC are well known. Moreover, a continuous range of solid solutions and pseudomorphic heterostructures of controlled periodicities and tunable band gaps from 2.3 eV (3C-SiC) to 6.3 eV (AlN) have been produced at North Carolina State University (NCSU) and elsewhere in the GaN-AlN and AlN-SiC systems. The wide band gaps of these materials and their strong atomic bonding have allowed the fabrication of high-power, high-frequency and high-temperature devices. However, the high vapor pressures of N and Si in the nitrides and SiC, respectively, force the use of low deposition temperatures with resultant inefficient chemisorption and reduced surface diffusion rates. The use of these low temperatures also increases the probability of the uncontrolled introduction of impurities as well as point, line and planar defects which are likely to be electrically active. An effective method must be found to routinely produce intrinsic epitaxial films of AlN, GaN and SiC having low defect densities.

Recently, Ceyer [1, 2] has demonstrated that the barrier to dissociative chemisorption of a reactant upon collision with a surface can be overcome by the translational energy of the incident molecule. Ceyer's explanation for this process is based upon a potential energy diagram (Fig. 1) similar to that given by classical transition-state theory (or activated-complex theory) in chemical kinetics. The dotted and dashed lines in Fig. 1 show, respectively, the potential wells for molecular physisorption and dissociative chemisorption onto the surface. In general, there will be an energy barrier to overcome for the atoms of the physisorbed molecule to dissociate and chemically bond to the surface. Depending upon the equilibrium positions and well depths of the physisorbed and chemisorbed states, the energy of the transition state  $E^*$  can be less than zero or greater than zero. In the former case, the reaction proceeds spontaneously. In the latter case, the molecule will never proceed from the physisorbed state (the precursor state) to the chemisorbed state unless an additional source of energy can be drawn upon to surmount the barrier. This energy can only come from either (1) the thermal energy of the surface, (2) stored internal energy (rotational and vibrational) of the molecule, or (3) the incident translational kinetic energy of the molecule. Conversion of translational kinetic energy into the required potential energy is the most efficient of these processes. Moreover, by adjusting the kinetic energy,  $E_i$ , of the incoming molecule, it is possible to turn off the reaction ( $E_i < E^*$ ), to tailor the reaction to just proceed ( $E_i = E^*$ ), or to set the amount of excess energy to be released ( $E_i > E^*$ ). The thrust of the present research is to employ these attributes of the beam translational energy to tune the reaction chemistry for wide band gap semiconductor epitaxial growth.

The transition state,  $E^*$ , is essentially the activation energy for dissociation and chemisorption of the incident molecules. Its exact magnitude is unknown, but is most certainly

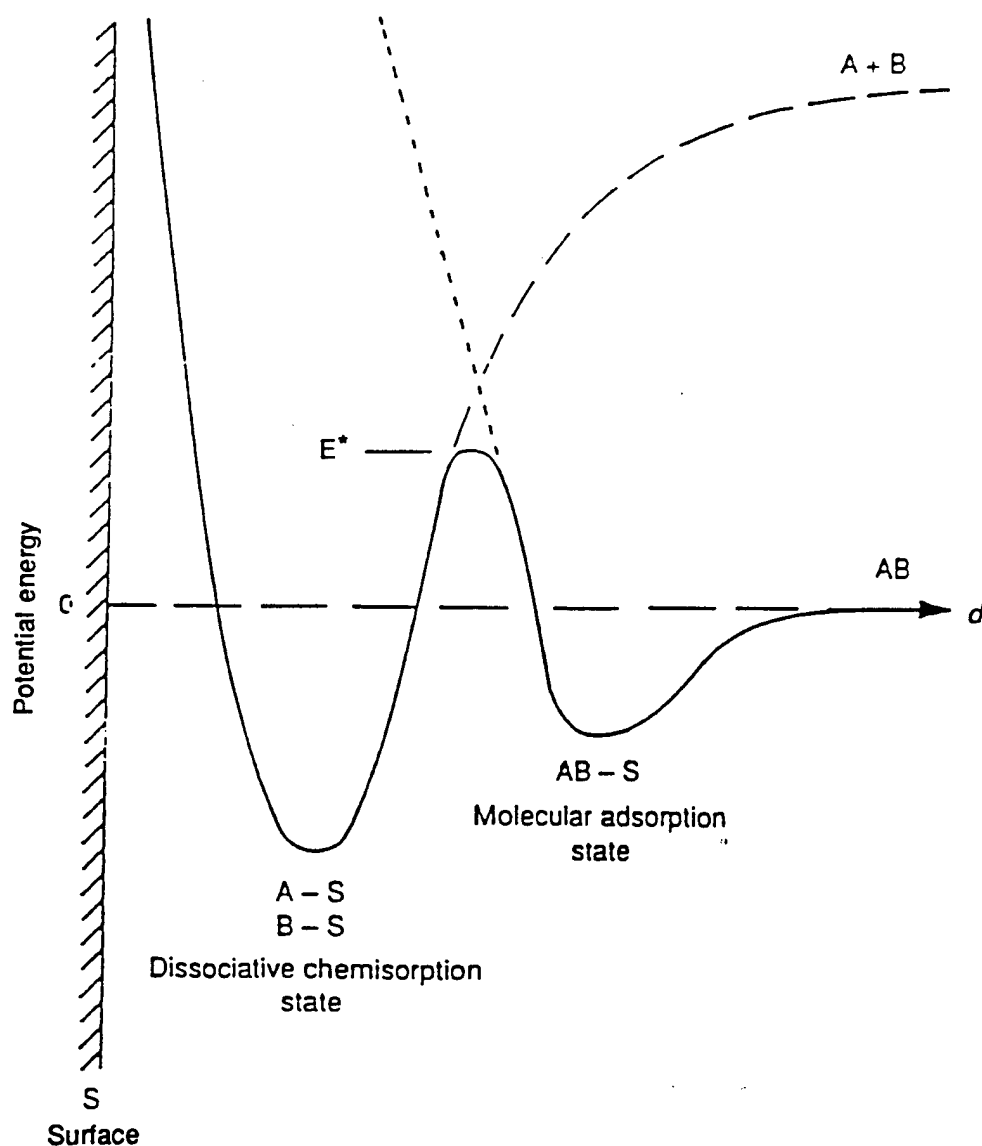


Figure 1. Schematic potential energy diagram of an activated surface reaction involving a molecularly physisorbed precursor state [from Ref. 1].

lower than the dissociation energy of the free molecule. It does not necessarily follow, however, that any kinetic energy above  $E^*$  will promote high-quality epitaxial growth of GaN. One must take into consideration another energy threshold,  $E_d$ , beyond which the kinetic energy of the incident flux will cause damage to the epitaxial film being synthesized. A typical  $E_d$  threshold value is approximately five times the band gap of the crystal and in the case of GaN,  $E_d \approx 18$  eV.

From the above consideration, it is clear that the key to high quality epitaxial growth is to be able to tune the energy of the incoming flux species over a range of energies defined by the window between  $E^*$  and  $E_d$ . Since the window is quite restrictive, i.e. 1-20 eV, it is essential that the energy spread of the flux species must be small, i.e. the flux species should ideally be

monoenergetic. To this end, we employ selected energy epitaxial deposition (SEED) systems for the growth of AlN, GaN and SiC wide band gap semiconductors. The SEED systems are of two types: (1) a seeded-beam supersonic free-jet (SSJ) and (2) a dual ion-beam Colutron. Both these SEED systems have the desirable property of a narrow energy spread of  $\leq 1$  eV.

Epitaxial growth using the seeded-beam SSJ involves a close collaboration between investigators at NCSU and Arizona State University (ASU). At ASU, the SSJ is interfaced directly into a low-energy electron microscope (LEEM) for the conduct of *in situ* studies of the nucleation and growth of epitaxial layers; while at NCSU, the SSJ systems are used to grow device-quality AlN, GaN and SiC for real applications. Exchanges in personnel (students) and information between the two groups ensures the achievement of desired results. The additional thin film growth experiments using dual-beam Colutrons and the theoretical studies referred to in this report are primarily conducted at ASU.

The research conducted in this reporting period and described in the following sections has been concerned with (1) epitaxial AlN films grown on 6H-SiC(0001) substrates using an ammonia supersonic seeded beam, (2) *in situ* LEEM/LEED studies of GaN homoepitaxial growth on MOCVD GaN substrates by plasma-assisted gas-source MBE, and (3) *in situ* cleaning of MOCVD-grown GaN/AlN/6H-SiC substrates using NH<sub>3</sub>-seeded supersonic molecular beams. The following individual sections detail the procedures, results, discussions of these results, conclusions and plans for future research. Each subsection is self-contained with its own figures, tables and references.

1. S. T. Ceyer, Langmuir 6, 82 (1990).
2. S. T. Ceyer, Science 249, 133 (1990).

## II. Influence of 6H-SiC(0001) Substrate Surface Morphology on the Growth of AlN Epitaxial Layers

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Epitaxial AlN films were grown on 6H-SiC(0001) substrates using an ammonia supersonic seeded beam. The films grown on substrates etched in hydrogen at high temperatures were shown by ion beam channeling to exhibit a higher degree of order relative to those grown on the as-received substrates. Cross-sectional electron microscopy revealed sharper SiC-AlN interfaces with extended flat terraces. In particular, very few stacking mismatch boundaries were observed to originate from the 1.5 nm steps which correspond to the 6H stacking sequence of the substrate.

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Aluminum nitride (AlN) is a candidate material for high-temperature, high-power microelectronics applications, as well as for negative electron affinity cold cathodes [1,2]. Aluminum nitride exhibits a direct band gap of 6.2 eV, a melting temperature of 2275°C and a thermal conductivity of 3.2 W/cmK [1]. The possibility of alloying AlN with gallium nitride (GaN), which has a direct band gap of 3.34 eV, leads to the development of a material system with potential optoelectronic applications extending to the deep ultraviolet wavelengths. Recently, AlN has been used as buffer layer for GaN growth on sapphire ( $\text{Al}_2\text{O}_3$ ) [3,4] and SiC [5] substrates. For example, it was shown that a thin AlN layer on  $\text{Al}_2\text{O}_3$  led to subsequent GaN layers with narrower band edge emission as examined by photoluminescence [3]. It was also reported that GaN layers grown on 6H-SiC(0001) were polycrystalline unless a monocrystalline AlN buffer layer was deposited first [5]. These factors provide strong motivation to investigate the parameters that lead to the growth of highly ordered, single crystalline AlN layers on 6H-SiC(0001). One of the critical issues that merit attention is a reduction in the density of threading defects in the AlN layer.

Defect densities of  $\sim 1 \times 10^{12} \text{ cm}^{-2}$  have been estimated for AlN grown on 6H-SiC (0001) [6]. Such high dislocation density was attributed to the high elastic moduli of these two materials and their thermal expansion mismatch since the lattice mismatch is only on the order of 1%. In addition, planar defects originating at step edges in the 6H-SiC (0001)-AlN interface were reported [7]. The defects were identified as interface domain boundaries (IDBs). Similar defects were reported [8] for GaN grown on non-isomorphic substrates: these were termed stacking mismatch boundaries (SMBs). As illustrated in Figs. 1(a) and 1(b), the latter type of defect is formed when two neighboring islands coalesce at a substrate step. Islands grown on adjacent SiC terraces display stacking sequences that are dictated by the respective stacking sequence of the underlying substrate. Upon coalescence, a mismatch boundary is produced, implying that stacking faults or dislocations parallel to the surface will be produced [7,8]. Conversely, mismatch boundaries should not form when the uppermost layers of adjacent terraces have the same underlying stacking sequence [8]. Therefore, if the step structure of the 6H-SiC(0001) substrate can be tailored such that all terraces have the same underlying stacking sequence, it should be possible to produce AlN layers with reduced defect densities.

As-received 6H-SiC (0001) substrates typically contain a distribution of steps with random terminations so that growth of AlN layers on these substrates leads to a high density of mismatch boundaries. In addition the as-received 6H-SiC (0001) substrates also contain high densities of surface defects and scratches due to mechanical polishing [9-11], which can lead to the formation of additional defects during AlN growth. There have been several reports on 6H-SiC(0001) surface treatments that have led to smooth, highly-structured surfaces with different step configurations. These treatments include: i) oxidation [12]; ii) etching in a  $\text{H}_2$  or



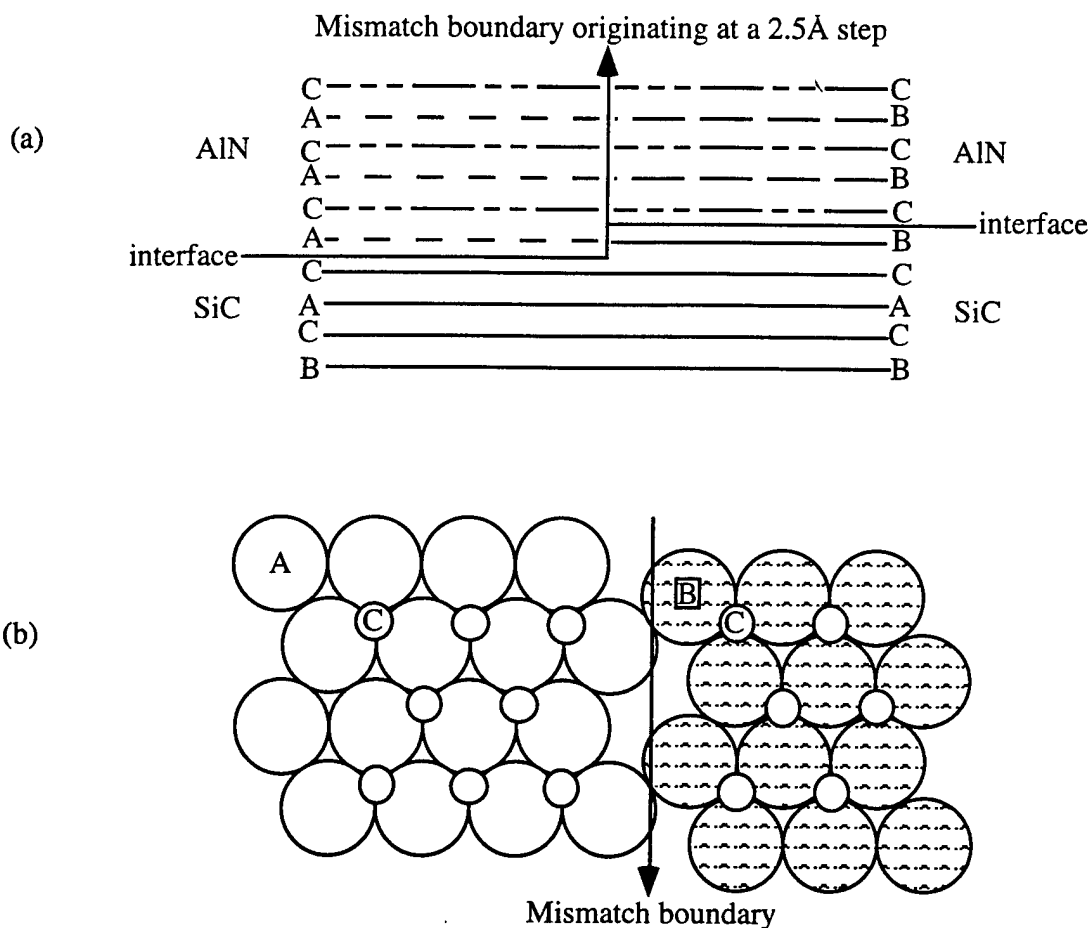


Figure 1. a) Cross sectional schematic of an AlN-SiC mismatch boundary originating from a  $2.5\text{\AA}$  step. Note the ..ACAC.. to ..BCBC.. stacking transition across the step site; (b) Top view schematic of a stacking mismatch boundary such as that depicted in (a). Note the ..ACAC.. to ..BCBC.. stacking mismatch across the boundary.

$\text{H}_2/\text{HCl}$  environment [11,13,14]; iii) sublimation etching [11]; and iv) chemomechanical polishing [10,15]. The high temperature, i.e.  $\sim 1600^\circ\text{C}$ , hydrogen etch has been reported to remove all surface scratches and leave a regularly stepped surface consisting of 1.5 nm steps along the c-axis consistent with the 6H stacking, i.e.  $6 \times 0.25\text{ nm}$  [11,14]. The other treatments remove scratches but display steps of varying heights. An atomic force microscope (AFM) image of a typical hydrogen-etched 6H-SiC(0001) surface is shown in Fig. 2. The surface displays flat terraces  $\sim 400\text{ nm}$  wide separated by steps of 1.5 nm in height. Since these regular 1.5 nm steps are terminated with the same stacking sequence, it might be anticipated that the density of mismatch boundaries in the AlN layers grown on such substrates should be reduced. To test this conjecture, we have conducted a comparative study of AlN layers grown on as-received and on hydrogen-etched 6H-SiC(0001) substrates.

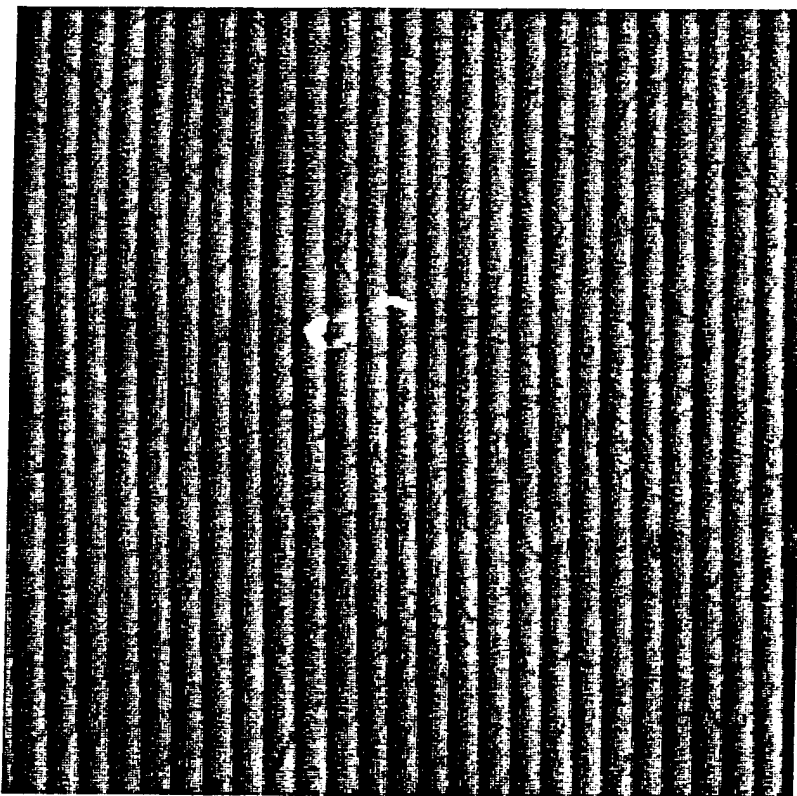


Figure 2. 6H-SiC(0001) substrate surface after hydrogen etching at 1600°C. Note the periodic steps and lack of surface scratches.

Silicon-terminated p-type 6H-SiC (0001) wafers (supplied by Cree Research, Inc.) were used as substrates. Prior to growth, the substrates were degreased in methanol, acetone and isopropanol for 5 minutes each, at a temperature of 65°C. The substrates were then dipped in a 10% HF aqueous solution for 15 min. to remove the oxide. In an alternate sample preparation procedure, the samples were etched at 1600°C in a mixture of 5% H<sub>2</sub> and 95% He for 15 min. following the 10% HF dip. This etching treatment was conducted at atmospheric pressure.

The AlN layers were grown in an ultrahigh vacuum deposition chamber using an Al evaporative cell and a helium supersonic beam seeded with NH<sub>3</sub> [6]. The chamber was evacuated by a cryo-trapped diffusion pump and baked at 150°C for ten hours. A base pressure of  $\sim 5 \times 10^{-10}$  Torr was obtained which increased to  $\sim 5 \times 10^{-9}$  Torr during deposition. The 6H-SiC(0001) substrates were degassed by heating to  $\sim 500^\circ\text{C}$  until the pressure dropped below  $1 \times 10^{-9}$  Torr. They were then annealed at 900°C for 20 min to remove oxygen and carbon contamination [16]. Auger electron spectroscopy depth profiles revealed an oxygen-free interface indicative of an initially clean surface. The AlN layers were grown at 900°C with an Al flux of  $2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$  and a NH<sub>3</sub> flux of  $3.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ . The supersonic jet source which provided the NH<sub>3</sub> flux has been previously described [6]. The deposition process lasted 60 min.

Scanning electron micrographs of the AlN surface revealed smooth continuous surfaces. Electron channeling patterns of the AlN and underlying 6H-SiC(0001) substrate exhibited six-fold symmetry consistent with the hexagonal symmetry of the AlN film and the 6H-SiC substrate oriented along the (0001) direction [6,17]. These results confirmed the epitaxial nature of the AlN layers.

Rutherford backscattering spectroscopy (RBS) was used to provide a quantitative measure of the perfection of the AlN layer. Figure 3 shows typical RBS spectra from an AlN layer on 6H-SiC(0001). Two spectra are shown, one where the RBS beam was aligned for channeling with the AlN epitaxial layer and one where the RBS beam was at a random orientation. RBS simulations of the random spectra show that the AlN film was stoichiometric with an areal density of  $2 \times 10^{17} \text{ cm}^{-2}$  (AlN) units equivalent to an estimated AlN layer thickness of  $\sim 50 \text{ nm}$ . Such a calculation assumes an AlN surface density of  $1 \times 10^{15}$  AlN units per  $\text{cm}^2$ . The ratio between the aligned and random Al peak was used as an indication of the crystalline quality of the film. This ratio is referred to as the minimum yield which is commonly abbreviated as  $\chi$ . Lower values of  $\chi$  correspond to increased crystalline order.

A total of twenty AlN films were grown on as-received and hydrogen-etched substrates. The quality of the layers was strongly dependent on the substrate treatment. The AlN layers grown on as-received substrates had an average  $\chi$  value of  $46\% \pm 32\%$  relative to  $17\% \pm 3.4\%$  for AlN grown on hydrogen-etched substrates. The lower average value of  $\chi$  for AlN layers grown on hydrogen-etched SiC samples is indicative of a higher degree of crystalline order. The broader distribution of  $\chi$  values for AlN layers grown on as-received substrates suggests

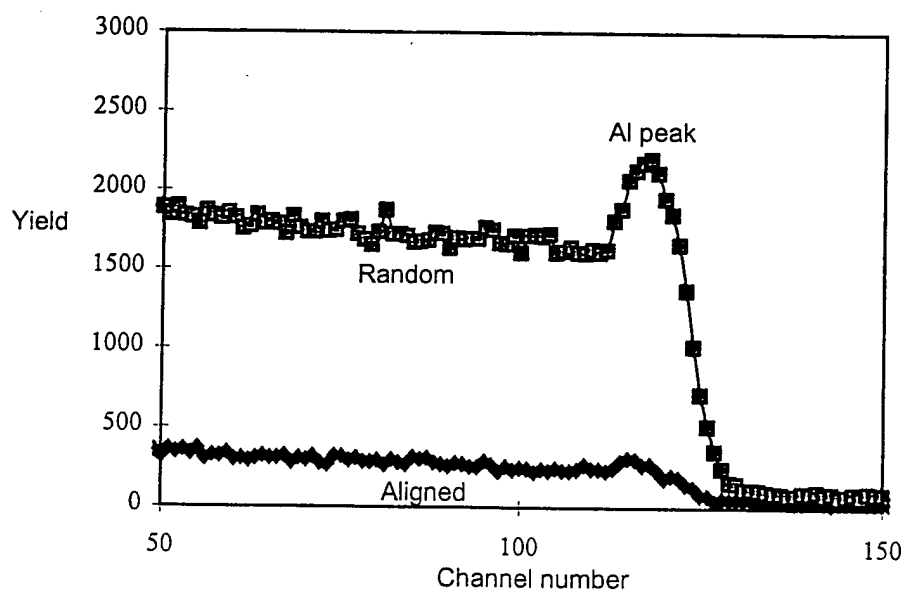


Figure 3. Rutherford backscattering spectra of an epitaxial AlN layer on a hydrogen etched 6H-SiC(0001) substrate exhibiting a  $\chi$  value of  $\sim 10\%$ .

that the surface morphology of these substrates vary substantially, probably as a result of inconsistent polishing procedures. The improvement in the standard deviation of  $\chi$  for AlN layers grown on hydrogen-etched substrates suggest better reproducibility of the substrate surface morphology. The difference between the values of  $\chi$  for the AlN layers grown on these two types of surfaces is significant to about 98% confidence.

Electron microscopy of cross-sectional samples was used in order to identify the origin of the difference in  $\chi$  values for the different AlN layers. Figures 4 (a) and 4(b) show examples of two typical electron micrographs of AlN layers grown on as-received and hydrogen-etched substrates, respectively. The ..ABCACB.. and ..ABAB.. stacking sequences for 6H-SiC(0001) and 2H-AlN(0001) are clearly visible in each micrograph. The AlN films grown on the as-received substrate display considerable disorder at the interface, as well as disordered regions in the bulk of the film. The AlN films grown on the hydrogen-etched substrate display a dramatically improved interface in conjunction with a higher degree of crystalline order. It seems likely that the disorder in the AlN layer grown on the as-received substrate originates from the disordered AlN-SiC interface.

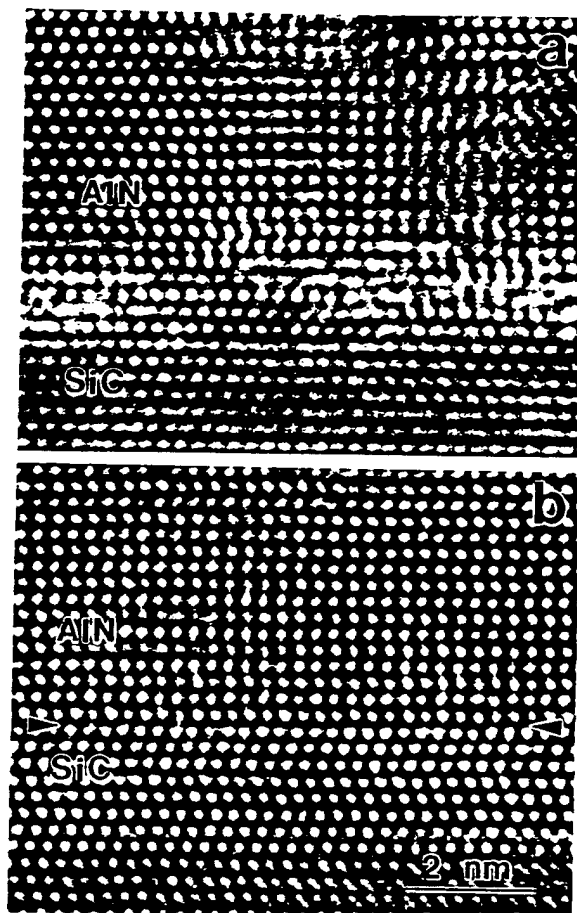


Figure 4 . High resolution electron micrograph comparing growth of AlN on (a) as-received, and (b) hydrogen etched, SiC substrates.

Figure 5 shows a representative electron micrograph of the AlN-SiC interface with a 1.5 nm step site on the hydrogen-etched substrate. The terraces on the substrate have the same termination and their step height of 1.5 nm corresponds to three (0001) lattice spacings of AlN, i.e.  $3 \times 0.498$  nm. When an AlN layer grown on the lower terrace coalesces with a layer grown on the upper terrace, they are effectively "in phase", i.e. the AlN layers terminate with the same atomic stacking sequence across the interface continuously. Thus, no mismatch boundary defects are formed.

In conclusion, a comparison of AlN films grown on as-received and high-temperature, hydrogen-etched 6H-SiC(0001) substrates confirms that a significant improvement in the film crystallinity can be achieved because the controlled step heights characteristic of the hydrogen-etched substrate surface lead to a reduction of stacking mismatch boundaries.

Electron microscopy was carried out in the Center for High Resolution Electron Microscopy at Arizona State University. The RBS characterization was carried out in the IBeam Laboratory at Arizona State University. This work was supported by the Office of Naval Research under Grant No. N00014-95-1-0122 and by the National Science Foundation MRSEC program DMR-9632635.

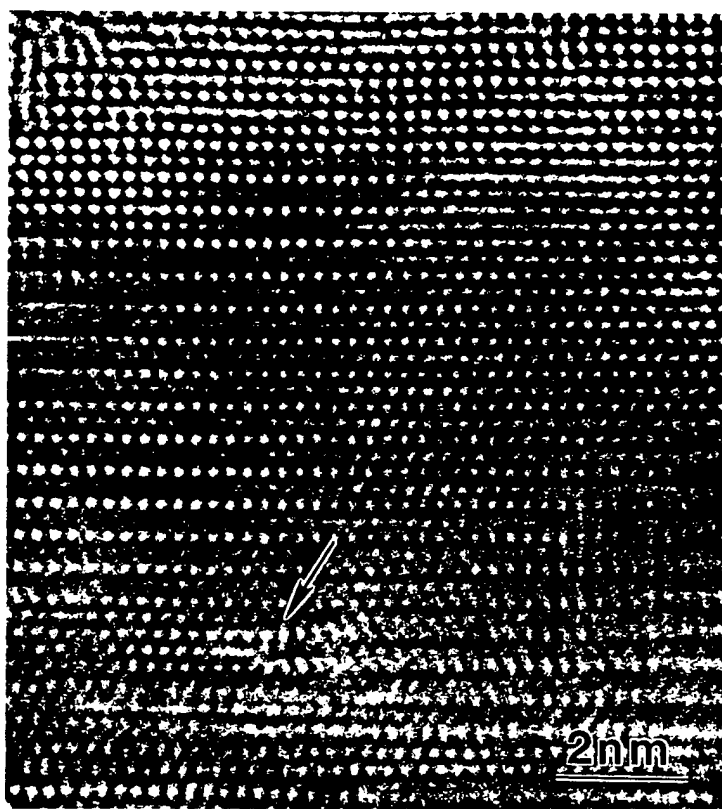


Figure 5. High resolution electron micrograph of the AlN-SiC interface with a 1.5 nm step site on a hydrogen etched substrate (see arrow).

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### III. LEEM/LEED Studies of GaN Homoepitaxy on GaN Substrates

Cleaning of the MOCVD GaN substrate with N atoms from a RF plasma N-atom source was described in the March 1998 quarterly report. In this series of growth experiments, the GaN substrate was heated at 675°C under a N-atom flux of  $\sim 0.35$  ML/min. After several minutes of N-atom treatment, the initial step contrast in the LEEM disappeared. Gallium was deposited on the substrate surface until the  $1\times 1$  LEED spots were considerably sharpened. GaN homoepitaxial growth was conducted on this surface at 660°C.

By maintaining a Ga flux 6–10 times higher than the N-atom flux, steps began to be visible after about 36 minutes of growth. After approximately 60 minutes, the parquet step structure similar to that shown in Fig. 1 appeared, but the contrast was poor. After 2.5 h deposition, the parquet step structure was clearly observed with good contrast and dark spots were visible on the surface. A clear  $1\times 1$  LEED pattern without any facet spots was observed after 3.0 h deposition. One notable aspect during the deposition was that the LEEM image brightened when the Ga flux was increased (by increasing the Ga crucible temperature), and the image darkened when the Ga flux was reduced. This possibly reflects the importance of maintaining a high Ga:N flux ratio to sustain basal plane growth which gave rise to a brighter (00) LEED spot.

After 6.0 h of growth the homoepitaxial GaN layer appeared (Fig. 1). The surface appeared to be flat with steps of atomic height arranged in a hexagonal parquet fashion. From the LEEM images, it was difficult to tell whether the dark spots were holes or protrusions or due to impurities. On another GaN layer grown in the LEEM for 6 hours, but was held at 660°C for 5 min. after the Ga and N fluxes were terminated, the hexagonal parquet steps became meandering.

After cooling to room temperature, the GaN homoepitaxial layer was removed from the LEEM and AFM imaging of the surface was conducted. The grown layer was found to be about 60 nm thick which implied a growth rate of  $\sim 10$  nm/h. The AFM image in Fig. 2(a) shows a  $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$  area and spiral crystals of hexagonal shape were clearly visible. The dark spots were holes or surface pits, with a density of about  $1\text{--}2 \times 10^{-9}$  cm $^{-2}$ . Although the pits appeared to be randomly distributed, they had the tendency of lying in regions where steps intersect or on step edges, see Fig. 2(b). They were almost never found to lie in the middle of a terrace. A high magnification AFM image (Fig. 2(c)) revealed that the holes or pits have a hexagonal shape. The hexagonal pit shape was especially distinct in the GaN homoepitaxial layer which was annealed for 5 min at the growth temperature of 660°C after the fluxes were turned off.

Our LEEM observations reported here were similar to the observations of hexagonal spiral growth and surface pits by Tarsa *et al.*[1] in their plasma-assisted GSMBE homoepitaxial growth of GaN. Our next series of homoepitaxial growth experiments will be conducted with the NH $_3$  seeded-beam supersonic jet (SSJ).

1. E.J. Tarsa *et al.*, J. Appl. Phys. **82**, 5472 (1997).

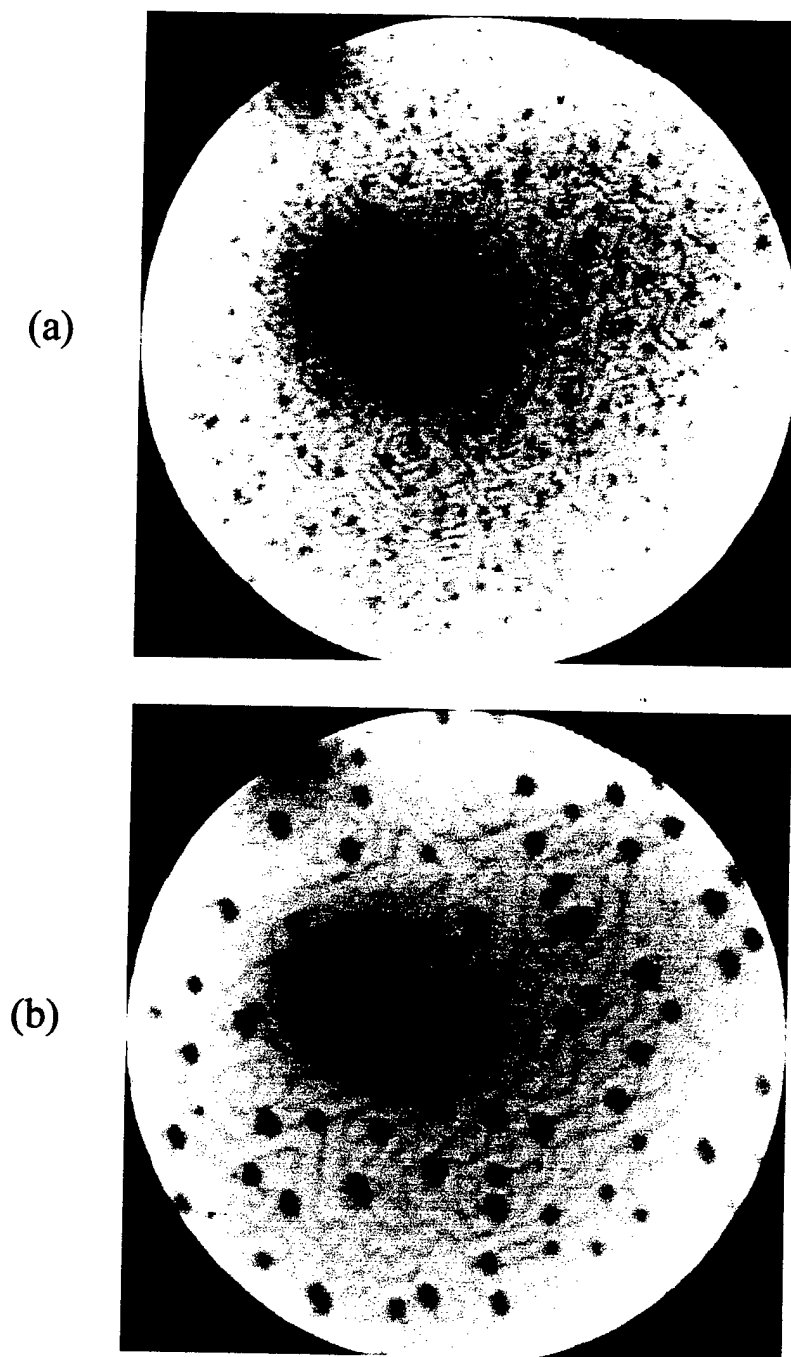
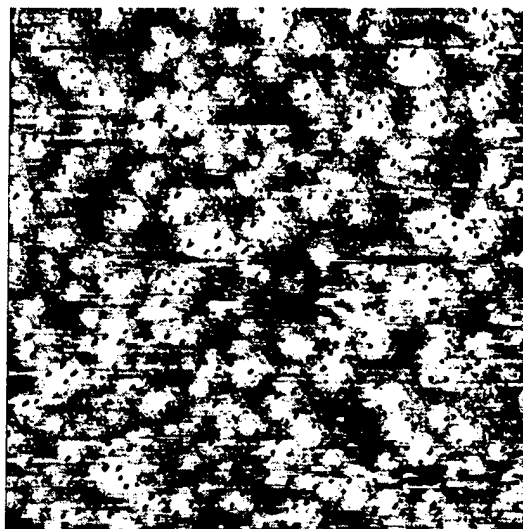


Figure 1. LEEM images of GaN homoepitaxially grown on MOCVD GaN substrates. Field of view (a) 4.8  $\mu\text{m}$  and (b) 2.0  $\mu\text{m}$ . Electron energy 2.0 eV. The large dark spot near the center of the image is an artifact due to damage of the channel plates by intense secondary emission from GaN.



(a)  
5 $\mu\text{m}$  x 5 $\mu\text{m}$



(b)  
1 $\mu\text{m}$  x 1 $\mu\text{m}$



(c)  
250nm x 250nm



Figure 2. AFM images of homoepitaxial GaN layers.

## IV. *In Situ* Cleaning of GaN using an Ammonia-seeded Supersonic Beam

### A. Introduction

Gallium nitride is a wide band gap semiconductor ( $E_g=3.4$  eV) with many potential optoelectronics and high-temperature, high-frequency, microelectronics applications. Gallium nitride forms a continuous range of solid solutions with AlN (6.28 eV) and InN (1.95 eV), permitting the fabrication, via band gap engineering, of laser diodes with tunable emission frequencies from covering the visible and UV regions. State-of-the-art GaN films ( $\leq 10^8$  defects per  $\text{cm}^2$ ) have been used to fabricate blue light emitting diodes (LEDs) and laser diodes.

Heteroepitaxial growth of high-quality monocrystalline GaN films has been problematic due to the lack of a suitable lattice-matched substrate and the thermodynamic instability of GaN under high-temperature growth conditions. Sapphire, the most common substrate, exhibits a 14% lattice mismatch at the GaN(0001)/sapphire(0001) interface; moreover, the thermal expansion coefficient of sapphire is 25% greater than that of GaN. Only by employing a low-temperature AlN or GaN buffer layer can one obtain monocrystalline GaN films on sapphire with defect densities in the  $10^8$ – $10^9$   $\text{cm}^{-2}$  range.

Substrate temperatures in excess of  $1000^\circ\text{C}$  are employed for growth of monocrystalline GaN films by halide or metal-organic CVD (MOCVD) using  $\text{NH}_3$ . In MOCVD, substrate thermal energy is used to overcome activation barriers for precursor decomposition and adatom surface migration (lateral diffusion); however, GaN decomposition above  $620^\circ\text{C}$  *in vacuo* necessitates the use of large V/III flux ratios [1]. Plasma-assisted processes have been utilized to lower the GaN growth temperature to approximately  $700^\circ\text{C}$ , but ion-induced damage and oxygen contamination is often observed.

The use of energetic neutral beams of precursor molecules is an alternative approach to the epitaxial growth of GaN films at lower substrate temperatures. In selected energy epitaxy (SEE), heavy reactant molecules are seeded in a supersonic expansion of light molecules and thereby accelerated to hyperthermal energies. The precursor molecules attain kinetic energies on the order of 1–2 eV that can provide the necessary energy for activated surface processes, such as dissociative chemisorption and adatom migration. Hence, in prospect, monocrystalline GaN films may be grown at lower substrate temperatures by SEE than by conventional MOCVD [2]. Moreover, energetic neutral beams with narrow energy distributions are ideal tools for fundamental studies of wide band gap semiconductor growth using *in situ* low-energy electron microscopy (LEEM) and other techniques.

To demonstrate the potential advantages of SEE, homoepitaxial growth of GaN on high-temperature MOCVD-grown GaN substrates is under investigation. This approach obviates the substrate lattice-mismatch issue, allowing the effects of precursor kinetic energy and film

morphology to be studied in isolation. It has become increasingly apparent, however, that in order to achieve 2-D, step flow growth methods for *in situ* substrate cleaning must be perfected. The previous report detailed results of *in situ* GaN cleaning using a seeded supersonic NH<sub>3</sub> beam. Modifications have been made to the SEE system to provide a cleaner vacuum ambient and are detailed in this report. The design of the N plasma source and testing chamber are also reported.

## B. Experimental Procedure

*SEED/XPS Deposition System.* The SEED/XPS multi-chamber system described in previous reports (June 1996, Dec. 1996) was used for *in situ* cleaning of GaN substrates. The orifice used in the NH<sub>3</sub> nozzle was 150 mm. A conical skimmer used for extracting the NH<sub>3</sub> beam from the supersonic free jet had an opening of 1 mm in diameter, a base of 20 mm in diameter, an included angle of 25° at the opening and of 70° at the base, and a height of 17 mm. The collimation aperture of 5×5 mm<sup>2</sup> was located downstream between the 2nd differential pumping stage and the growth chamber. The molecular beam was directed to the substrate with an incident angle of 6° with respect to the surface normal. The deposition area on the vertical substrate was 15×15 mm<sup>2</sup>.

*Substrate Preparation/Cleaning.* The substrates were 0.5-μm thick GaN films grown by MOVPE on on-axis 6H-SiC employing a 0.1-μm thick AlN buffer layer. The substrates were provided by D. Thomson and O.-H. Nam of Prof. Davis group and used as received. Ag paste was used to provide good thermal contact between the Mo sample holder and the GaN/AlN/6H-SiC substrate; two Mo pins were used to hold the substrate in place. The Mo holder was placed on a hot plate to dry the Ag paste for 5 min at 80°C. Subsequently, it was introduced via the load-lock chamber and transferred *in vacuo* into the growth chamber. The sample was heated slowly to 400°C under a NH<sub>3</sub> flux for outgassing. Prior to the growth, the GaN substrate was cleaned *in situ* by NH<sub>3</sub> beam exposure at 730°C for 30 min, unless otherwise noted. After *in situ* cleaning, the substrate temperature was lowered to 200°C under an NH<sub>3</sub> flux. The GaN substrate was examined by *in situ* RHEED before and after cleaning, as well as by on-line XPS to determine the surface carbon and oxygen concentrations. The procedures used for RHEED and XPS were described in previous reports.

## C. Results and Discussion

*In Situ Substrate Cleaning Using a Seeded Supersonic NH<sub>3</sub> Beam.* GaN substrates were cleaned using different temperatures and times in order to pinpoint the source of oxygen and carbon contamination in the system. The surfaces of the as-received substrates contained 9–14% oxygen and 12–19% carbon contamination, as evidenced by XPS. As noted in the previous report, oxygen can be thermally desorbed in vacuum. Complete oxygen removal was

achieved by outgassing the substrate at 400°C for 60 min and then heating at 730°C for 60 min, as evidenced by the XPS spectra in Fig. 1.

As illustrated in Fig. 1, carbon contamination increased during heating in vacuum. It is believed this is due to outgassing of the colloidal Ag paste that was used to improve thermal contact between the substrate and the Mo sample holder. A new substrate holder was fabricated that used Mo clips and a polished Mo block to ensure good thermal contact without Ag paste. Pyrometer readings of the substrate and the Mo block indicated that the new holder provided thermal contact equivalent to that achieved previously using Ag paste. The new holder will be used in all future cleaning and growth experiments.

A quadrupole mass spectrometer (QMS) was installed in the deposition chamber and employed for residual gas analysis. The major residual contaminants after an 15 hour bake-out were CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O. There were also small peaks in the 26–30 amu range which were indicative of hydrocarbon contamination. QMS sampling indicated that there was no contamination entering the deposition chamber from the source chamber. Current effort is focused on identifying and eliminating contamination sources in the deposition chamber.

A new gas line has been installed to provide a Kr-seeded He supersonic beam for cleaning. A beam of hyperthermal Kr atoms will be used in conjunction with an NH<sub>3</sub> beam to remove surface contaminants. A 1.1 eV Kr beam will be generated by expanding 1% Kr in He through

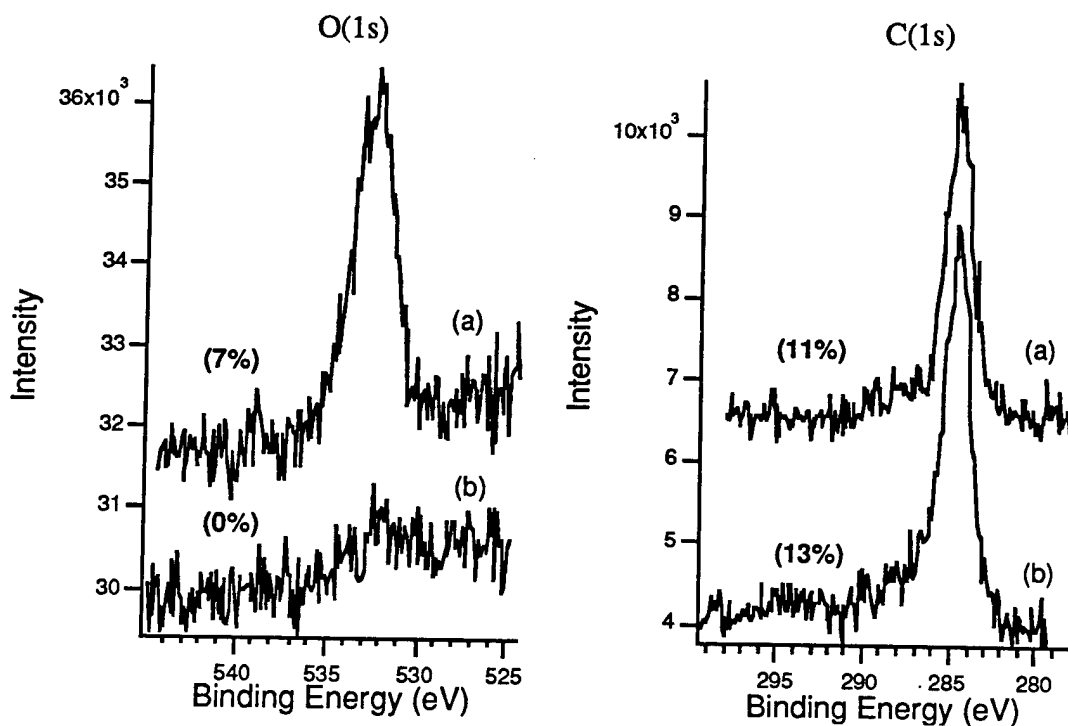


Figure 1. XPS Results of oxygen removal from GaN at 730°C: (a) GaN substrate before heating, (b) after heating at 730°C for 60 min.

a 25°C nozzle. In prospect, the Kr atoms will impart energy to surface contaminants allowing them to be desorbed at lower temperatures. RHEED and AFM of the substrate will be done to verify that energetic Kr atoms do not damage the smooth stepped surface. XPS of the films will be done to determine percent contamination.

*Supersonic Nitrogen Plasma Source.* A RF nitrogen plasma source that will produce active N species with controlled kinetic energies is under construction. A vacuum system equipped with time of flight equipment, a quadrupole mass spectrometer and optical emission spectrometer is being built to characterize the nitrogen plasma source (Fig. 2).

The nozzle design builds on the work of J. E. Pollard [5] and C. B. Mullins [6]. The coaxial resonator is designed with the appropriate shield diameter and coil diameter for operation at 13.56 MHz (Fig. 3). Progress on the construction of the system includes maintenance and repair of the appropriate mechanical and diffusion pumps, and machining of the nozzle components.

#### E. Future Plans

Once we have succeeded in producing smooth, atomically clean GaN substrates, a more detailed investigation of GaN homoepitaxial growth using dual  $\text{NH}_3$  and TEG supersonic beams will be done to elucidate the relationships between film quality and precursor kinetic energies tuned by seeded supersonic beams. Results from the growth of relatively smooth films using the Ga K-cell will be used to estimate the Ga flux needed to grow smooth films using a supersonic TEG beam. Comparisons will be made between the  $\text{NH}_3$  kinetic energy effect on growth rate and film morphology and TEG kinetic energy effects.

An Al Knudsen cell will be installed in the system, enabling us to examine the growth of AlN using supersonic beams of  $\text{NH}_3$  and N. The Al Knudsen cell will also be used to grow buffer layers for heteroepitaxial growth of GaN on SiC substrates. A cold-lip Al K-cell, Model EPI-20-Al equipped with a 20-cc PBN crucible, a water-cooled shroud, rotary motion shutter

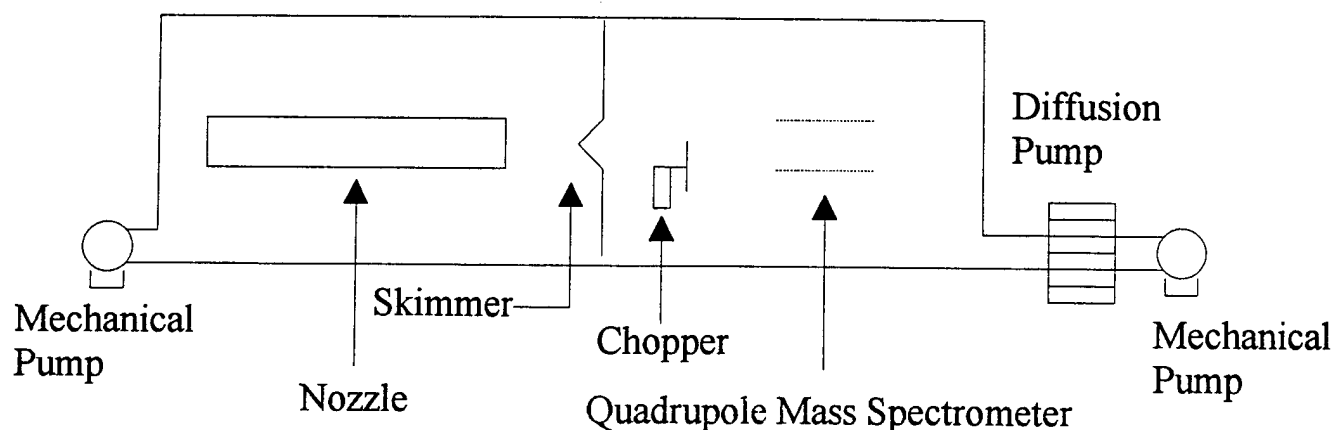


Figure 2. RF nitrogen plasma nozzle system schematic.

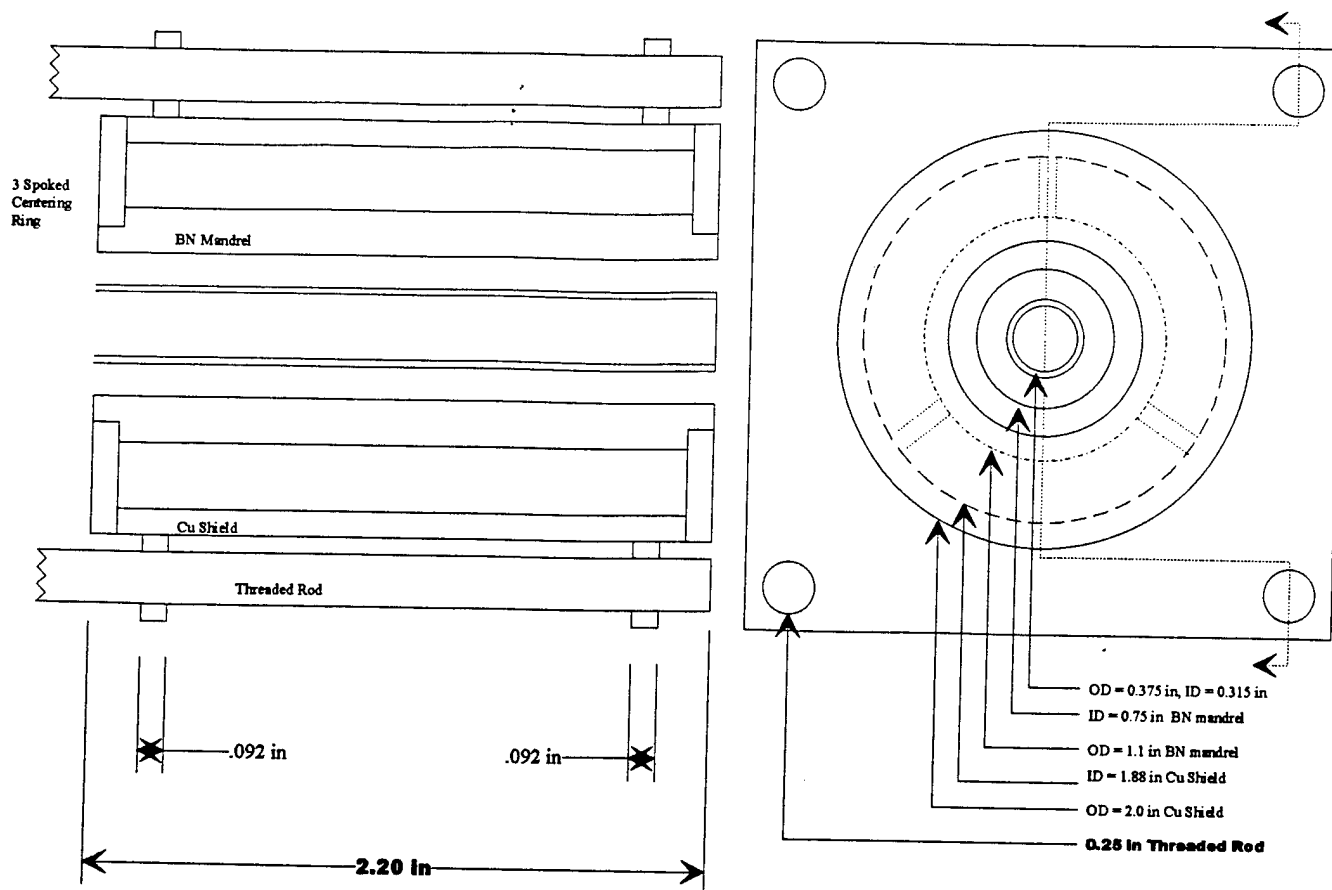


Figure 3. RF nitrogen plasma source.

and a Type C (W/Re 5/26%) thermocouple is on order. The thermocouple is equipped with a Tantalum sheath for use in an ammonia environment. The K-cell will be mounted on a 4.5 in. flange, and the lip of the crucible is ~5 in. from the substrate.

The active N species produced by the supersonic N plasma source will be characterized by QMS and optical emission spectroscopy (OES). QMS will be used to determine the  $N_2$  dissociation efficiency by measuring the atomic N content of the beam. OES will be used to detect and characterize various active N species (e.g. N,  $N_2^+$  and  $N_2^*$ ) via analysis of specific electronic transitions involving excited state species. The kinetic energy distribution of atomic N species will be determined by time-of-flight measurements.

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